
**HEAT AND MASS TRANSFER
IN HETEROGENEOUS CATALYSIS. XXX.*****EFFECT OF HEAT
AND MASS TRANSFER AT THE EXTERNAL SURFACE
OF THE CATALYST PARTICLE ON BEHAVIOUR
OF AN ISOTHERMAL TUBULAR FLOW REACTOR**

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On a mathematical model is studied the effect of heat and mass transfer between the external surface of the catalyst particle and the bulk of the reaction mixture on dynamic behaviour and on steady states of the isothermal tubular flow reactor. The model was considered for the plug flow reactor. It was found that with a strongly exothermic reaction, when in a certain interval of conversions of the reactant two stable steady states of the catalyst particle may exist, the dependence of conversion on the reactor length in steady state was dependent on the way the reactor was brought into the steady state. Examples are presented and discussed of dynamic behaviour of the reactor at a change of partial pressure of the reactant and at a change of feed rate of the reaction mixture into the reactor.

In preceding papers the effect of heat and mass transfer between the external surface of the catalyst particle and the bulk of the reaction mixture on steady states¹ and on dynamic behaviour of the catalyst particle² was studied. It was determined that heat and mass transfer between the external surface of the catalyst particle and the bulk of the reaction mixture (further on called the external heat and mass transfer) significantly affects the reaction rate in a steady state. With exothermic reactions there can, at certain conditions, exist at a single value of partial pressure of the reactant and temperature in the bulk of the reaction mixture, two steady states of the catalyst particle. Further it was determined that the rate with which the catalyst particle approaches the steady state is dependent on partial pressure of the reactant. Aim of this work is to study consequences of effects of the external heat and mass transfer on steady states and on dynamic behaviour of the tubular flow reactor in which the bulk of the reaction mixture has a constant temperature and the temperature of the external surface of the catalyst particle is variable. This isothermal reac-

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tor is a certain idealisation for strongly exothermic reactions, because it is necessary to anticipate existence of temperature fields even in the bulk of the reaction mixture.

THEORETICAL

Reaction rate is a function of partial pressure of the reactant and of temperature of external surface of the catalyst particle. For calculation was used the equation

$$r_R = k \exp [E(T_s - T)/RT_s T] p_{A_s}. \quad (1)$$

The transfer rate of matter *A* from the bulk of the reaction mixture toward the surface of the catalyst particle was expressed by relation

$$r_D = k_g a_m (p_A - p_{A_s}). \quad (2)$$

The heat transfer rate from the external surface of the catalyst particle into the bulk of the reaction mixture was expressed by relation

$$r_h = k_h a_m (T_s - T). \quad (3)$$

It is assumed that the catalyst particle has in all points the same temperature as is the temperature of the external surface (particle with a high thermal conductivity). Differential equation expressing changes in the particle temperature then has the form

$$r_R(-\Delta H) = k_h a_m (T_s - T) + c_{pk}(\partial T_s / \partial t)_{x,z}. \quad (4)$$

The derivation was made at the assumption that the possible mass accumulation in particles is far smaller than the heat accumulation, *i.e.* that the rate of mass transfer of component *A* to the particle surface always equals the reaction rate, which may be expressed as

$$r_R = r_D. \quad (5)$$

Material balance in the tubular flow reactor with plug flow is expressed by equation

$$F p_{A0}(\partial x / \partial z)_{T_s, t} - p_{A0} S \varepsilon (\partial x / \partial t)_{T_s, z} = r_R (1 - \varepsilon) S \gamma_k R T. \quad (6)$$

Equations (4) and (6) were for calculations transformed into dimensionless forms

$$\varepsilon (\partial x / \partial \tau)_{\Delta T, Z} = (\partial x / \partial Z)_{\Delta T, \tau} - R \beta \text{Da}, \quad (7)$$

$$\varepsilon (\partial \Delta T / \partial \tau)_{x, Z} = B \text{Da} (R \beta - \Delta T / (\Phi_m \Omega_m)), \quad (8)$$

with the initial condition

$$\begin{aligned} \tau = 0 \quad \text{for } Z = 0 \quad \text{is } x = 0, \quad \Delta T = \Delta T_{in}, \\ \text{for } Z = 1 \quad \text{is } x = x_{in}, \quad \Delta T = \Delta T_{in} \end{aligned} \quad (8a)$$

and with boundary conditions for the case of a steady state

$$\tau = \tau_u \quad (\partial x / \partial \tau)_{\Delta T, Z} = (\partial \Delta T / \partial \tau)_{x, Z} = 0, \quad (8b)$$

$$\begin{aligned} \text{for } Z = 0 \quad \text{is } x = 0, \quad \Delta T = \Delta T_u, \\ \text{for } Z = 1 \quad \text{is } x = x_u, \quad \Delta T = \Delta T_u. \end{aligned} \quad (8c)$$

In Eq. (7) and (8) ΔT denotes the dimensionless temperature difference between the surface of the catalyst particle and the bulk of the reaction mixture, given by

$$\Delta T = (T_s - T)/T, \quad (9)$$

where τ is the dimensionless time defined by relation

$$\tau = tF/V \quad (10)$$

and Z the dimensionless length of the reactor, given by

$$Z = z/L. \quad (11)$$

B and Da are parameters defined by relations

$$B = p_{A0} V (-\Delta H) \varepsilon / (RT^2 W_{c, pk}), \quad (12)$$

$$Da = r_{om} WRT / (p_{A0} F). \quad (13)$$

If the catalyst particle is in a steady state the condition (5) must be fulfilled, together with the condition

$$r_h = r_R(-\Delta H), \quad (14)$$

from which follows that the reaction rate in steady state is determined by relation

$$R\beta = (P_{A0}(1-x) - R\beta\Phi_m) \exp [\Theta \Delta T / (1 + \Delta T)]. \quad (15)$$

RESULTS AND DISCUSSION

Physical Meaning of Dimensionless Parameters

The steady states of the isothermal tubular flow reactor are described by Eq. (7) and (8) in which are used three dimensionless parameters Φ_m , Ω_m , and Da . The steady states of the reactor are further dependent on the form of the kinetic equation, but this work is limited to the case of the first order reaction. Parameter Ω_m gives^{1,2} the largest temperature difference between the particle surface and the bulk of reaction mixture divided by the temperature of the bulk of reaction mixture, parameter Φ_m is^{1,2} the ratio of the reaction rate at partial pressure of the reactant on the particle surface, which equals to standard partial pressure and the surface temperature equals to the bulk temperature of the reaction mixture, to the greatest possible mass

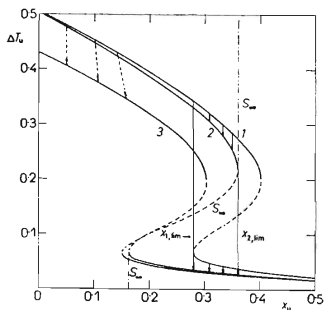


FIG. 1

Dependence of Catalyst Particle Temperature on Degree of Conversion of Reactant in Steady State

Dashed line denotes unstable steady states of the particle, solid arrows denote the course of steadying of the particle regime after a change of feed rate of reactant into reactor, dashed arrows after a change of partial pressure of reactant at the reactor inlet for $B = \infty$, Dash and dot line denotes the separatrix for $B = \infty$, $\Theta = 20.42$, $\Omega_m = 0.5165$; 1 $\Phi_m = 0.061$, $P_{A0} = 1$, 2 $\Phi_m = 0.050$, $P_{A0} = 1$, 3 $\Phi_m = 0.061$, $P_{A0} = 0.86$.

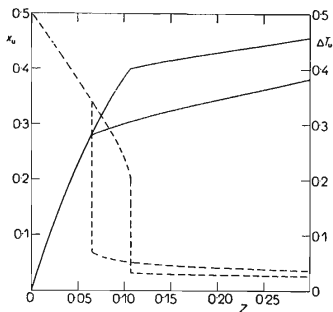


FIG. 2

Dependence of Degree of Conversion of Reactant and of Catalyst Particle Temperature on the Reactor Length in Steady State

Solid line denotes the dependence of degree of conversion, dashed line the particle temperatures. $\Phi_m = 0.061$, $P_{A0} = 1$, $Da = 0.319$ (curve 1 in Fig. 1).

transfer rate of component A toward the particle surface under given hydrodynamic conditions and at standard partial pressure of this component in the bulk of the reaction mixture. This parameter is a coordinate which determines the distance of the particle regime from the kinetic region when the effect of external heat and mass transfer is eliminated. Value of parameter Ω_m and Φ_m is determined by properties of the chemical reaction and by hydrodynamic conditions; provided the hydrodynamic conditions are constant this value is neither dependent on the reactor load and its volume nor on the degree of dilution of the catalyst by the inert material.

Da is the modified Damköhler number (reciprocal value of dimensionless load of the reactor). It is possible to consider it as a degree of conversion of the reactant which would have been achieved if the reaction had taken place in a single flow mixed reactor with an eliminated effect of external heat and mass transfer. Value Da determines the reactor load and varies from zero to one. This number determines the final degree of conversion in the reactor.

All mentioned parameters determine the steady state into which the reactor can be brought, however, they do not include quantities which affect the dynamic behaviour of the reactor. These quantities are collected in the constant B . This constant can be interpreted as a dimensionless temperature difference $\Delta T/T$, by which would change the temperature of the catalyst particle if the catalyst has received the heat liberated by reaction of the reaction mixture in the reactor at partial pressure of the reactant p_{A0} up to the degree of conversion equal to one. Value of this constant is dependent on ratio of the void volume of the reactor V_ε to the amount of catalyst, because with the increasing void volume increases the capability of the reactor to accumulate the reactant. Value of the constant B can be increased for inst. by diluting the catalyst with inert material.

Steady States of a Tubular Flow Reactor With Plug Flow

For strongly exothermic reactions in a certain region of conversions of the reactant two stable steady states of the catalyst particle can exist (Fig. 1). Since it is assumed in the considered model that the particles are not affecting each other, in this conversion region can generally each catalyst particle operate in one of two possible states. By an analysis limited to steady states of catalyst particles is not possible to determine explicitly the dependence of conversion on the reactor length in the steady state. It is only possible to determine two limiting longitudinal profiles of conversions in between which actual profile must be situated. One limiting profile corresponds to a case when all particles operate in a steady state with a lower reaction rate (lower steady states), the second limiting profile to a case when all particles operate in a steady state with a greater reaction rate (upper steady states). Calculation of these limiting steady states for the reactor with plug flow can be made by calculating the dependence of reaction rate from relation (15) and then by integration of relation

$$Da Z = \int_0^x R \beta^{-1} dx, \quad (16)$$

which follows from Eq. (7) for steady state. Examples of dependence of conversion and of temperature of the catalyst particle on the reactor length for two possible limiting cases are given in Figs (2) to (5). These dependences were obtained by numerical integration of Eq. (16) by Runge-Kutte method (Merson modification) on the digital computer Elliott 4100.

At the given assumptions in the reactor can be set as many conversion profiles as there are catalyst particles which can operate in two stable steady states. Which of the possible profiles will be steady depends on the way in which is the reactor brought into the steady state. For this reason several typical situations which can occur in the reactor are further studied.

Limiting Regimes of Steadying

Dynamic behaviour of the reactor is dependent on values of constant B , i.e. on the ratio of "capacity of the reactor void volume" to the "catalyst capacity". If the

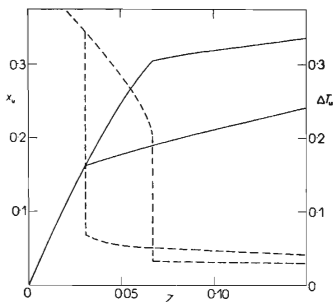


FIG. 3

Dependence of Degree of Conversion of Reactant and of Catalyst Particle Temperature on the Reactor Length in Steady State $\Phi_m = 0.061$, $P_{A0} = 0.86$, $Da = 0.3708$ (curve 3 in Fig. 1). Other symbols used are the same as those in Fig. 2.

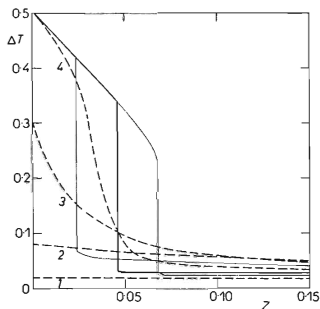


FIG. 4

Dependence of Degree of Conversion of Reactant on Reactor Length in Steady State and During Steadying into this Steady State for $B = 0$

Solid line denotes dependences corresponding to steady state, dashed line during steadying. $\Phi_m = 0.05$, $P_{A0} = 1$, $Da = 0.3595$ (curve 2 in Fig. 1); $1 \tau_m = 0.02$, $2 \ 0.15$, $3 \ 0.25$, $4 \ 0.35$.

value of this constant is very small (capacity of the void volume is small) then the conversion in the reactor volume must considerably change in order to cause the change in the particle temperature. The reactor is then steadied under conditions when the volume of the reactor is, because of minute particle state, practically in steady state (pseudostationary state of the volume). This means that the conversion in the

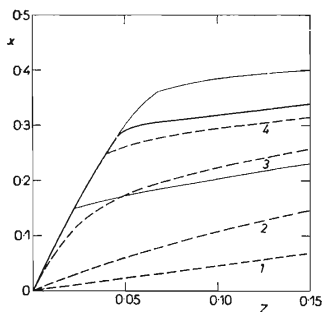


FIG. 5
Dependence of Catalyst Particle Temperature on Reactor Length in Steady State and During Steadying into this Steady State for $B = 0$
Symbols used are the same as those in Fig. 4.

volume always corresponds to the steady state of the reactor at instantaneous temperature of the particles. The course of steadying of the regime is then determined mostly by the rate of temperature steadying of individual catalyst particles. In this case it is possible to neglect the mass accumulation in the reactor and the system of Eq. (7) and (8) simplifies to

$$(\partial x / \partial \tau)_{\Delta T, z} = 0, \quad (17)$$

$$(\partial x / \partial z)_{\Delta T, \tau_m} = R\beta \text{ Da}, \quad (18)$$

$$\varepsilon(\partial \Delta T / \partial \tau_m)_{x, z} = \text{Da}(R\beta - \Delta T / \Phi_m \Omega_m). \quad (19)$$

In Eq. (18) and (19) is $\tau_m = \tau B$. Equations were solved numerically by the net method according to the explicite pattern.

In the second limiting case is the value of constant B high, *i.e.* the capacity of the reactor void volume is far greater than is the thermal capacity of the catalyst. In this case the particle temperature steadies much more quickly than partial pressure in the

reactor volume and in the time interval necessary for steadying of the particle temperature, partial pressure in the bulk of the reaction mixture does not practically change. The course of steadying of the reactor regime is then determined first of all by steadying of the partial pressure in the volume. Every dynamic process is started by a quick transformation of the particle temperature to the value corresponding to the steady state at the instantaneous partial pressure in the reactor, which is then followed by a slow change of temperature along the curve of steady state of the particle, *i.e.* along the curve $R\beta_u$ (pseudostationary state of the catalyst particle). Relation (8) can be simplified into a form

$$R\beta_u = \Delta T_u / (\Phi_m \Omega_m) \quad (20)$$

and for the reaction rate at any instant is valid relation (15). In such case it can be easily estimated into which state the catalyst particle will settle. If the temperature of the particle is greater in the moment before the made change than the temperature of unstable steady state, then the state of the particle would settle in the upper steady state; if it is lower, then it would settle in the lower steady state.

Estimation of Steady State of the Reactor for $B \rightarrow \infty$

If the state of the catalyst particle steadies immediately, it is a step change from one state to another in the moment of change of conditions around the particle. The course of steadying was studied for the case when the feed rate of the reaction mixture into the reactor is changed as well as for the case when is changed the partial pressure of reactant under constant hydrodynamic conditions and constant feed rate. The latter case can occur for inst. at catalytic oxidation and hydrogenation, when the reactant is present in the reaction mixture only in such small quantity that the change in partial pressure does not practically affect the flow rate or the physical properties of the reaction mixture.

Change of partial pressure of the reactant. Let us assume that the reactor is in a steady state at a single value of partial pressure of the reactant and that the partial pressure of the feed entering the reactor is changed. Then with a successive feeding of new reaction mixture into the reactor the partial pressure around each particle changes by a step change and a step change of the particle state from one to another takes place. A new steady state can be estimated by the following procedure:

We plot the dependence of degree of conversion on the reactor length in the original steady state. For each degree of conversion from the dependence $R\beta_u$, respectively ΔT_u on x can be determined the corresponding value of the reaction rate and the particle temperature in the original steady state. Further we calculate the dependence of reaction rate, degree of conversion and particle temperature on the reactor length in a new steady state. Simultaneously it is necessary to calculate also the particle temperatures corresponding in each point of the reactor to stable steady state which

forms a separatrix separating two stable steady states. The calculation should be made from the reactor inlet, and in the region in which two steady states exist it is necessary to use for calculation that steady state of the particle which is situated on the same side of the separatrix as the original state. Example of steady states at a change of partial pressure of the reactant in the reaction mixture entering the reactor is given in Fig. 6.

Change of feed rate of the reaction mixture into the reactor. At a change of feed rate, the values of parameter Φ_m and Da are changed while the value of parameter Ω_m changes only slightly. This means that the reaction course is expressed by another curve of dependence of the reaction rate and temperature of the catalyst particle on degree of conversion than by the curve before the change of feed rate. At the change of feed rate, the particle state changes immediately into the steady state at constant value of the degree of conversion, *i.e.* at the degree of conversion before the change of feed rate. So it can be determined into which steady state the particle will get when

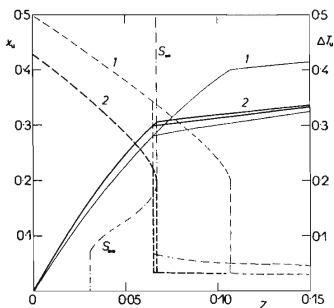


FIG. 6

Dependence of Degree of Conversion of Reactant and of Catalyst Particle Temperature on Reactor Length in Steady State after a Change of Partial Pressure of Reactant at the Reactor Inlet from Value 1 to 0.86 for $B = \infty$

Solid line denotes the dependence of degree of conversion, dashed line the particle temperature, dash and dot line the separatrix. $\Phi_m = 0.061$; 1 state before the change, 2 state after the change of partial pressure.

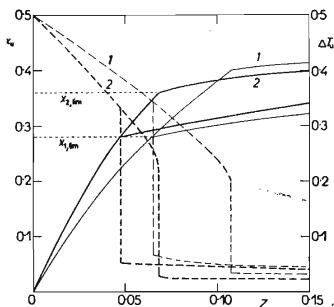


FIG. 7

Dependence of Degree of Conversion of Reactant and of Catalyst Particle Temperature on Reactor Length in Steady State after a Feed Rate Change of Reaction Mixture into the Reactor, or after a Change of Parameter Φ_m from Value 0.061 to 0.050 for $B = \infty$

$P_{A0} = 1$; other symbols used are the same as those in Fig. 6.

we plot the degree of conversion in dependence on the reaction rate $R\beta_u$ and on the particle temperature ΔT_u in steady state for both values of the feed rate (Fig. 7). From the result follows that at the beginning of the reaction, *i.e.* in the case when the partial pressure of the reactant in the reactor at the beginning of the dynamic process is null and the particle temperature equals to the bulk temperature of the reaction mixture, the particle regime steadies into a state with smaller reaction rate. At changes made during the operation of the reactor either the profiles can be set in which are all particles in the upper steady state or in the lower steady state or profiles in which a part of the particles operate in the lower and part in the upper steady states.

Estimate of the steady state of the reactor for $B = 0$. If the partial pressure of the reactant steadies in the reactor volume immediately, it is necessary to determine the steadying process by solving the system of Eq. (18) and (19). The steadying process was studied for the case when the feed rate of the reaction mixture into the reactor was changed, as well as for the case when was changed the partial pressure of the reactant in the reaction mixture at the reactor inlet.

Change of partial pressure of the reactant. At the start of the reaction *i.e.* in the case when at the beginning of the dynamic process the partial pressure of the reactant

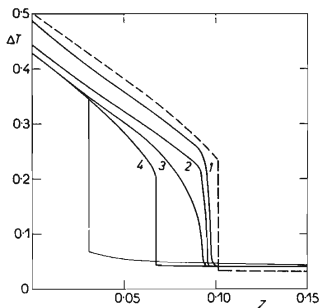


FIG. 8

Course of Steadying of Catalyst Particle Temperature after a Change of Partial Pressure of Reactant at the Reactor Inlet from Value 1 to 0.86 for $B = 0$

Dashed line denotes the state before the change, solid line the steadying course. $\phi_m = 0.061$; 1 $\tau_m = 0.01$, 2 0.05, 3 0.25, 4 the new state.

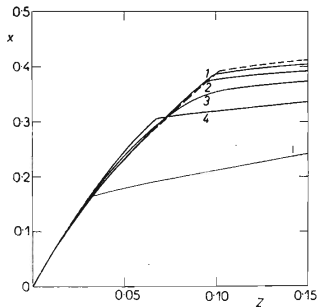


FIG. 9

Course of Steadying of Degree of Conversion of Reactant for the Case Given in Fig. 8

in the reactor is null and the particle temperature equals to the bulk temperature of the reaction mixture, the particle regime steadies in the upper steady states unlike when the value of constant B is very large. When this steady state was used as a initial state of the other dynamic changes, the state always steadies on those profiles in which all catalyst particles operate in the upper steady state. Even if the result cannot be considered an unique proof that the reactor state always passes at the value of constant $B = 0$ to the profile corresponding to the upper steady states, it is obvious that it can be anticipated in this case that profiles in which particles operate in the upper steady state will be attainable far easier and will be more probably the result of dynamic process than the profiles in which particles operate in the lower steady states. Examples of the steadying course of the degree of conversion and temperature of the catalyst particle are given in Fig. 8 and 9.

Change of the feed rate of the reaction mixture into the reactor. Results of calculation led to the conclusion that even in the case of change of feed rate the reactor regime steadies for value of constant $B = 0$ only on profiles in which all particles operate in the upper steady state. Examples of the steadying course of degree of conversion and of catalyst particle temperature are given in Fig. 10 and 11.

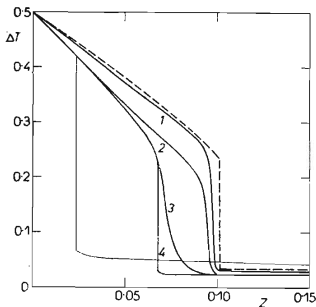


FIG. 10

Course of Steadying of Catalyst Particle Temperature after a Change of Feed Rate of Reactant into the Reactor, or after the Change of Parameter ϕ_m from Value 0.061 to 0.05 for $B = 0$

$P_{A0} = 1$; Other symbols used are the same as those in Fig. 8.

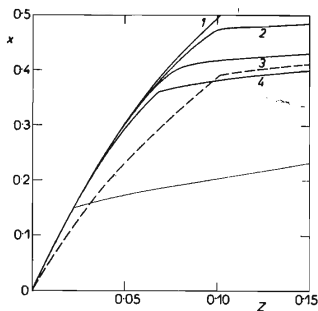


FIG. 11

Course of Steadying of Degree of Conversion of Reactant for Case given in Fig. 10

Symbols used are the same as those in Fig. 8.

TABLE I

Estimation of Actual Values of Constant B for Hydrogenation and Oxidation [Eq. (12)] $W/V = 800 \text{ kg/m}^3$, $\epsilon = 0.35$, $c_{pk} = 0.15 \text{ kcal/kg } ^\circ\text{K}$, $(-\Delta H) = 100 \text{ kcal/mol}$, $T = 473^\circ\text{K}$ for hydrogenation, $T = 623^\circ\text{K}$ for oxidation.

P_{A0} atm	Hydrogenation	Oxidation
0.05	0.0008	0.0005
1	0.0200	0.0090
100	1.6000	0.9000

CONCLUSIONS

From the results of calculations follows that values of constant B , which is determined by ratio of capacity of the reactor void volume to the catalyst capacity may effect the resulting profile of the degree of conversion and particle temperature to which the state of reactor will pass. For instance at the start of the reaction the reactor regime changes to the profile with the lower states of the particle at value of constant $B = \infty$ and to the profile with upper states of the particle at $B = 0$. Calculation of values of constant B for reaction conditions usual in tubular reactors has proved that practically under any conditions the capacity of the reactor void volume is so small that value of this constant can be assumed to be zero (Table I). In real reactors can be therefore expected that dynamic processes take place in such a way that partial pressure of the reactant in the reactor steadies practically immediately as compared to the temperature of the catalyst particle. The course of the dynamic process is therefore determined by the course of temperature changes of the catalyst particle and the reactor regime steadies on the profile in which all particles operate in the upper steady state.

LIST OF SYMBOLS

a_m	external surface of particles per unit mass of catalyst
B	constant defined by Eq. (12)
c_{pk}	specific heat of catalyst
Da	Damköhler number [Eq. (13)]
E	activation energy of reaction
F	volumetric feed rate of reaction mixture into the reactor
k	rate constant at temperature T
k_g	mass transfer coefficient
k_h	heat transfer coefficient
L	length of reactor
P_A	partial pressure of component A in bulk of reaction mixture

p_{Am}	standard partial pressure of component A in bulk of reaction mixture
p_{As}	partial pressure of component A on surface of catalyst particle
$P_A = p_A/p_{Am}$	dimensionless partial pressure of component A
r_D	mass transfer rate [Eq.(2)]
r_h	heat transfer rate [Eq. (3)]
r_{Om}	reaction rate at temperature T and at partial pressure p_{Am} at conditions when the effect of external heat and mass transfer is eliminated
r_R	reaction rate [Eq. (1)]
$R\beta = r_R/r_{Om}$	dimensionless reaction rate [Eq. (15)]
R	gas constant
s_∞	separatrix for $B = \infty$
S	cross-sectional area of the reactor tube
t	time
T	temperature of the bulk of reaction mixture
T_s	temperature of the catalyst particle surface
v	volume of reactor
W	weight of catalyst
x	degree of conversion of reactant
$x_{1,lim}, x_{2,lim}$	limiting values of degree of conversion, at which for a change of feed rate of reaction mixture into the reactor a step change of particle regime from diffusion branch of curve $R\beta_v$ to the kinetic one takes place
z	distance from the reactor inlet in the direction of axial reactor axis
Z	dimensionless distance [Eq.(11)]
γ_k	specific weight of catalyst
ΔH	enthalpy of reaction
ΔT	dimensionless temperature difference [Eq. (9)]
ε	relative void volume of the reactor
$\Theta = E/(RT)$	dimensionless parameter
τ	dimensionless time Eq. (10)]
$\tau_m = \tau B$	modified dimensionless time
$\Phi_m = r_{Om}/(k_g a_m p_{Am})$	dimensionless parameter
$\Omega_m = (-\Delta H)k_g p_{Am}/Tk_h$	dimensionless parameter

Subscripts

- u steady state
 o state corresponding to the reactor inlet
 in initial state

REFERENCES

- Horák J., Jiráček F.: This Journal 35, 174 (1970).
- Horák J., Jiráček F.: This Journal, in press.

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